

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

FILE
cop-1

(12) UK Patent Application (19) GB (11) 2 098 222 A

(21) Application No 8213166
(22) Date of filing 6 May 1982
(30) Priority data
(31) 8113987
(32) 7 May 1981
(33) United Kingdom (GB)
(43) Application published
17 Nov 1982
(51) INT CL³
C08C 1/14
(52) Domestic classification
C3L BC
C3W 113 213
(56) Documents cited
None
(58) Field of search
C3L
(71) Applicants
Malaysia Rubber
Research Institute,
P.O. Box 150, Kuala
Lumpur, Malaysia
(72) Inventors
John Charrappathanathu
Kuruvilla,
Chan Boon Lye,
Abdul Latiff Bin Abdul
Majid
(74) Agents
Stevens, Hewlett and
Perkins,
5 Quality Court, Chancery
Lane, London WC2A 1HZ

(54) Processing of hevea latex

(57) The invention relates to a method of producing solid coagulated natural rubber which comprises:

1. ammoniating field latex to a pH of at least 9.0;
2. stabilizing the ammoniated latex with a nonionic surface active agent;
3. fermenting the ammoniated latex for a period of at least 3 days under anaerobic conditions;
4. before, or during fermentation

treating the ammoniated, stabilized latex with at least one proteolytic enzyme;

5. during the fermentation and enzymatic treatment maintaining the pH of the latex at at least 9.0 if necessary by further additions of ammonia;

6. optionally, diluting the fermented and enzymatically treated latex with water; and

7. coagulating the latex with acid.

GB 2 098 222 A

SPECIFICATION

Processing of hevea latex

The present invention relates to the processing of *Hevea* latex into dry rubber and in particular to the processing of field latex into dry rubber.

5 *Hevea* latex contains substances other than rubber and water, the major non-rubber components being protein, lipids and quebrachitol. The protein content of field latex is approximately 1% of the weight of latex. About 20% of the protein is adsorbed on the rubber particles and stabilises them, about 20% is associated with the 'bottom' fraction and the remainder is dissolved in the aqueous (serum) phase. Although some non-rubbers can be advantageous to the finished rubber the presence of protein does not confer any significant advantage and it can adversely affect the dynamic properties. Recent 10 investigations have shown that steam coagulated rubber with relatively high protein and ash contents has low dynamic properties, while biologically coagulated or surfactant coagulated rubber with low protein and ash contents has better dynamic properties. For certain applications, particularly those where the heat build-up properties are important, consumers prefer rubber with low protein content.

15 Various methods have been suggested in the past to produce rubber with less protein. One method is to repeatedly centrifuge field latex and dilute the resulting concentrate, but this is cumbersome, time consuming and costly. Another method is to coagulate field latex with an anionic surfactant, such as dioctyl sodium sulposuccinate, usually at neutral pH, but it is difficult to apply to ammoniated field latex as coagulation is extremely slow at alkaline pH, particularly above pH 8. This 20 method has not been adopted commercially because of its inapplicability to ammoniated latex. A third method is to treat centrifuged concentrated latex with an alkaline protease, subsequently diluting to 5% dry rubber content (drc) and coagulating the diluted latex with an acid. This process has also not met with commercial success, mainly because it is cumbersome and costly. Recently it has been reported that a low nitrogen rubber with improved dynamic properties can be obtained by coagulating field latex with a proteolytic enzyme such as papain; but the process has not been commercially adopted. In all 25 these prior art proposals the latex either as field or concentrated latex was coagulated either during or within a short time after the particular treatment without allowing it to undergo any extended period of microbial or enzymic fermentation.

30 The present invention is based on the discovery that by fermenting ammoniated and preferably stabilized field latex through microbial and enzymic treatments followed by acid coagulation with or without prior dilution, the resulting rubber has unexpectedly low nitrogen and ash contents and improved dynamic properties, particularly heat build-up properties.

The present invention accordingly provides a method of producing solid coagulated natural rubber which comprises:

- 35 1. ammoniating field latex, preferably freshly tapped field latex, to a pH of at least 9.0 and preferably about 9.5;
2. stabilizing the ammoniated latex with a nonionic surface active agent;
3. fermenting the ammoniated latex for a period of at least 3 days under anaerobic conditions;
4. before, or during fermentation treating the ammoniated, stabilized latex with at least one 40 proteolytic enzyme;
5. during the fermentation and enzymatic treatment maintaining the pH of the latex at at least 9.0 and preferably at about 9.5, if necessary by further additions of ammonia;
6. optionally diluting the fermented and enzymatically treated latex with water; and
7. coagulating the latex with acid.

45 The first step in the method of the invention is that field latex is ammoniated to a pH of at least 9.0 and preferably about 9.5. This typically involves an initial addition of from 0.1 to 1% by weight of ammonia based on the dry rubber content (drc) of the latex, the precise amount varying according to the particular sample of latex. At pHs less than 9.0 the beneficial effects of the invention tend to be diminished and particular care may be needed to avoid premature coagulation. At pHs above about 9.5 50 microbial activity is reduced and requires larger additions of ammonia adding to the cost. Preferably the pH used is not more than about 9.5. Also, since the method involves acid coagulation such higher pHs necessitate the use of larger amounts of acid on coagulation. The field latex is preferably freshly tapped field latex. More particularly it is preferred that the latex is treated according to the invention within 24 hours of tapping. Specifically it is preferred that the fermentation step, described below, commences 55 within 24 hours and optimally within 8 hours of tapping.

A nonionic surface active agent is also added to the latex to enhance its stability. The preferred surface active agents are the condensation products of an alkylene oxide, especially ethylene oxide, with a lipophilic component. The lipophilic component is typically the residue of a fatty alcohol, a fatty acid or an alkyl phenol, among fatty alcohols and fatty acids those having from 10 to 20 carbon atoms per 60 molecule are preferred with those having C₈ to C₁₈ carbon chains being especially preferred. The chain can be straight or branched chain and saturated or unsaturated. Among alkyl phenols those having C₈ to C₁₀ alkyl groups are preferred. The number of alkylene oxide residues condensed with the lipophilic component will typically be in the range 15 to 100, although higher numbers may be used if desired. To avoid clouding during processing in rubber-growing countries, the cloud point of the surface active

agent is preferably above 50°C. Specific examples of suitable surface active agents include ethylene oxide condensation products of nonyl phenol such as those sold under the trade name Nonidet, in particular Nonidet P—40.

5 The amount of surface active agent is chosen to impart adequate stability. The use of less than 0.05% by weight on the drc of the latex is not usually adequately effective and use of more than 5% by weight on the drc of the latex generally provides no further advantage and adds to costs. We have obtained optimum results by using amounts of surface active agent in the range 0.5 to 1.0% by weight on the drc of the latex. 5

10 Preferably, the latex is stabilized with the surface active agent prior to fermentation. In this case the surface active agent will usually be added to previously ammoniated latex. Since, as is described below the presence of proteolytic enzyme in the latex during fermentation has a destabilising effect on the latex, in this case the surface active agent is added to the latex prior to fermentation and preferably prior to addition of the proteolytic enzyme. Additionally in this case, in view of the extended period of fermentation it is desirable to employ an enhanced concentration of surface active agent, particularly about 0.75% by weight based on the drc of the latex. 10 15

15 The ammoniated and preferably also stabilised latex is fermented for a period of at least 3 days. In the fermentation it will not usually be necessary to add the specific microorganisms active during fermentation since these are present in the normal microflora in tapped field latex. Latex in healthy rubber trees is sterile but is rapidly contaminated by a wide spectrum of microorganisms on and after tapping. However, "seeding" of the latex may be carried out if desired, as described below. The microorganisms, especially bacteria, in the tapped latex feed on the non-rubbers in the latex and in particular, at least initially, on the sugars and produce acids thus lowering the pH of the latex. To avoid coagulation of the latex by the acid produced by the bacteria, the pH of the latex is maintained at at least 9.0 throughout the fermentation, if necessary by further addition(s) of ammonia. This maintenance of pH is similar to the technique described in our earlier British Patent Specification No. 1293176. 20 25 25 Preferably the fermentation is carried out for at least 5 days and fermentation over a period of 7 days is especially preferred because it enables the invention to be carried out on a weekly cycle. Longer fermentation periods are possible but, particularly if extended beyond 15 days, involve substantial further costs in the provision of suitable storage facilities.

30 In addition to the fermentation step, the latex is treated using a proteolytic enzyme. This treatment can be effected before, or preferably, during the fermentation. Since the presence of the enzyme destabilizes the latex to some extent (e.f. the prior art use of papain to coagulate latex) treatment during fermentation necessitates additional care to avoid premature coagulation and usually rather higher amounts of surface active agent, as is mentioned above, will be used. (When the enzyme is added to the latex prior to fermentation it will normally continue its activity during fermentation.) Less enzyme is 35 35 needed when enzymatic proteolysis takes place during fermentation as compared with when the enzyme is added after fermentation.

40 The particular source of the proteolytic enzyme does not appear to be critical and we have successfully tested proteolytic enzymes from plant sources e.g. papain (obtained by drying milk tapped from immature fruits of *Carica papaya*) and bacterial sources e.g. Alcalase (a protein derived from bacteria of the genus *Bacillus*, manufactured by Novo Industry) and Suprase (a commercial subtilisin, manufacture by Pfizer.). 40

45 The amount of enzyme used will normally be in the range of 0.01 to 0.3%, optimally 0.05%, of 100% active enzyme by weight based on the drc of the latex. The length of time of the enzyme treatment is preferably at least 6 hours. This can readily be achieved when the enzyme treatment is started during fermentation (and automatically when the enzyme is present in the latex throughout fermentation). 45

50 After fermentation and enzyme treatment the latex is coagulated by addition of acid. Typically coagulation is effected by lowering the pH of the latex to about 5 using a strong acid such as sulphuric or formic acid. Acid coagulation is conventional in the art. Optionally prior to coagulation the latex may be diluted. It is a specific advantage of the present invention that it is possible to obtain solid rubber having both low protein and ash contents without prior dilution. However, moderate dilution e.g. to about 10% rubber solids (field latex as tapped containing about 30% rubber solids) by weight enables solid rubber of even lower ash content to be obtained, the protein content being lowered slightly. 55 55 Dilution prior to coagulation increases the amount of acid needed to effect coagulation and increases the volume of the latex to be handled during coagulation. The extent of dilution used in any particular case will depend on the balance between the reduction in ash and the increase in cost. Generally, in this invention the latex will not be diluted more than five-fold i.e. to a content of rubber solids of about 6% and preferably not more than about 3-fold, as mentioned above. This represents an advantage over prior techniques where a ten-fold dilution to 3% rubber solids sometimes followed by centrifuging and re-dilution was necessary to obtain even fairly limited reduction in protein and ash contents. 60 60

65 It is a particularly advantageous feature of this invention that it can readily be operated over a weekly (or other similar) cycle. This possibility is a separate aspect of the invention. Accordingly, the invention includes a method of making solid coagulated natural rubber which comprises the steps of: 65 1. bulking a portion of freshly tapped field latex which has been ammoniated to a pH of at least

- 9.0, stabilized with a non-ionic surface active agent and treated with a proteolytic enzyme;
2. repeating step 1 on a daily basis for at least 5 and preferably 7 days thereby allowing the bulked latex to ferment;
3. maintaining the pH of the bulked latex at at least 9.0, if necessary by adding further ammonia;
- 5 4. on a subsequent day, removing from the fermented bulk a portion of the latex and coagulating 5 it, optionally after dilution, with acid, and replacing the latex removed from the bulk with a further portion of freshly tapped field latex treated according to step 1; and
5. repeat step 4 on a daily basis.
- An alternative to this method comprises the steps of:
- 10 1. bulking a quantity of at least 5 and preferably 7 portions of latex which has been ammoniated to 10 a pH of at least 9.0, stabilized with a non-ionic surface active agent and treated with a proteolytic enzyme;
2. holding the bulked latex for at least the same number of days as portions of latex in it, thereby allowing the latex to ferment;
- 15 3. maintaining the pH of the latex at at least 9.0, if necessary by adding further ammonia; 15
4. on a subsequent day, removing from the fermented bulk a portion of the latex and coagulating it, optionally after dilution, with acid, and replacing the latex removed from the bulk with a portion of freshly tapped field latex treated according to step 1; and
5. repeating step 4 on a daily basis.
- 20 In these two techniques the average fermentation time of the latex is a function of the size ratio of the 20 daily portion to the bulk, although it may take some time for the average time to become settled. As is indicated the preferred time cycle is a weekly one, corresponding to a bulk of seven times daily production.
- These cyclical techniques have the advantages that day-to-day variation in the properties of the 25 rubber and minor variations in the daily yield are evened out. Further a well established fermentation 25 bulk contains a flourishing population of the microorganisms which bring about the desired changes in the latex thus accelerating the beneficial effects of the fermentation.
- Additional to the steps set about above the rubber may be treated by other techniques to provide desired properties. For example, the rubber, as latex or solid rubber may be treated with hydroxylamine, 30 preferably as neutral acid addition salt, to stabilize its (Mooney) viscosity or with oxalic acid and thiourea 30 to enhance retention of plasticity.
- The following Examples illustrate the invention. Examples 1, 2 and 3 show the effect of individual steps and are not of the invention. Examples 4 to 6 show the beneficial effect of combining the individual steps in the method of the invention. In the Examples all percentages measuring quantities of 35 material are by weight and, with reference to adding material to latex, are by weight on the drc of the 35 latex.

EXAMPLE 1

Field latex ammoniated to pH 9.5 was kept in a closed container for 28 days and allowed to ferment. The pH was maintained by periodic addition of ammonia solution as necessary. The latex 40 remained fluid throughout the experiment. At various intervals latex samples were withdrawn, 40 coagulated with formic acid at pH 5.0 and the resulting dry rubber tested for nitrogen and ash contents. The results are given in Table 1.

TABLE 1

Age of latex (day)	Nitrogen (%)	Ash (%)
1	0.45	0.31
7	0.45	0.17
10	0.42	0.21
14	0.41	0.15
21	0.41	0.18
28	0.40	0.21

There was no difficulty in coagulating the latex on the first day but on subsequent days, particularly after 7 days, coagulation was incomplete with loss of rubber. It was also observed that mere microbial fermentation of latex did not reduce the nitrogen to any appreciable extent. However, the ash content fell significantly over the first week.

5 EXAMPLE 2

Field latex was ammoniated to pH 9.5 and fermented for 28 days as described in Example 1. At various intervals samples of fermented latex were withdrawn from the bulk and treated with proteases (Papain, Suprase, Alcalase) shortly before coagulation with formic acid at pH 5.0. The solid rubber was tested for nitrogen and ash and the results are given in Table 2. As a result of the enzyme treatment about 24% reduction in nitrogen levels was obtained and all three enzymes behaved similarly. Prolonged fermentation did not further reduce the nitrogen indicating that the effect of enzyme treatment on the fermented and fresh field latices is the same.

TABLE 2

Age of latex (days)	Papain %	Suprase %	Alcalase %	Nitrogen %	Ash %
0	—	—	—	0.41	0.36
7	—	—	—	0.42	0.13
28	—	—	—	0.37	0.15
0	0.2	—	—	0.24	0.22
7	0.2	—	—	0.28	0.19
28	0.2	—	—	0.28	0.18
0	—	0.2	—	0.28	0.20
7	—	0.2	—	0.32	0.17
28	—	0.2	—	0.34	0.16
0	—	—	0.2	0.37	0.19
7	—	—	0.2	0.32	0.16
28	—	—	0.2	0.32	0.19

EXAMPLE 3

15 A bulk of field latex was ammoniated to a pH 9.5 and allowed to ferment for 7 days. On the eighth day one seventh of the fermented latex was withdrawn and an equal quantity of fresh latex ammoniated to pH 9.5 was added, keeping the volume of the bulk the same. The procedure was continued for 28 days; whenever necessary, ammonia was added to maintain the pH. At various intervals samples were drawn from the bulk and were further treated with proteolytic enzymes and coagulated as described in Example 2. The resulting dry-rubber was tested for nitrogen and ash contents and the results are given in Table 3.

TABLE 3

Age of latex (days)	Papain (%)	Suprase (%)	Alcalase (%)	Nitrogen (%)	Ash (%)
1 (control)	—	—	—	0.40	0.30
21	0.2	—	—	0.24	0.15
28	0.2	—	—	0.17	0.10
21	—	0.2	—	0.20	0.24
28	—	0.2	—	0.19	0.18
21	—	—	0.2	0.24	0.18
28	—	—	0.2	0.17	0.19

It can be seen that cycling of latex using a 7 day retention in the fermentation reduces nitrogen levels by up to 50%. All the three enzymes behaved similarly.

EXAMPLE 4

- 5 Field latex was ammoniated to pH 9.5 and allowed to ferment for 7 days. On the eighth day the fermented latex was treated with Papain or Alcalase with or without the addition of Nonidet-P40 and with or without diluting the latex as shown in Table 4. The solid rubber produced after subsequent coagulation was tested for nitrogen and ash. The presence of the surface active agent gave enhanced ash reduction both in the diluted and undiluted latex systems. It did not reduce the nitrogen level in the latex treated with Papain but there was slight reduction in the Alcalase treated system. Dilution of the latex to a drc of 10% scarcely affected the nitrogen level but it markedly reduced the ash, particularly when the latex was treated with Nonidet-P40 and enzyme.
- 10

TABLE 4

DRC %	Papain %	Alcalase %	Nonidet %	Nitrogen %	Ash %
30	—	—	—	0.40	0.18
10	—	—	—	0.37	0.08
30	0.2	—	—	0.16	0.24
10	0.2	—	—	0.14	0.16
30	—	0.2	—	0.23	0.21
10	—	0.2	—	0.20	0.12
30	0.2	—	0.5	0.13	0.19
10	0.2	—	0.5	0.14	0.15
30	—	0.2	0.5	0.18	0.16
10	—	0.2	0.5	0.15	0.10

In Examples 2, 3 and 4 the enzyme treatment was carried out outside the fermentor, i.e. the fermented latex was withdrawn from the fermentor and then treated with the enzyme prior to its coagulation with acid. Experiments were carried out to find out whether it is possible to reduce the enzyme concentration using a prolonged treatment. Field latex was therefore fermented at pH 9.5 as in example 1 without cycling and further treated with Nonidet-P40 and Alcalase. the range of Nonidet-P40 tested was 0.05% to 5% and that of the Alcalase 0.01% to 3.0%. Small samples of treated latex was withdrawn at various intervals and tested for fluidity. The resulting dry rubber was tested for nitrogen and ash. The results obtained are set out in Table 5.

TABLE 5

Nonidet (%)	Alcalase (%)	Fluidity (days) *	Nitrogen (%)	Ash (%)
Nil	Nil	> 50	0.46	0.09
	0.01	> 50	0.14	0.17
	0.025	14	0.12	0.25
	0.05	8	0.11	0.46
	0.10	5	0.13	0.41
	0.20	3	0.09	0.39
0.5	Nil	> 50	0.44	0.08
	0.01	> 50	0.13	0.06
	0.025	18	0.09	0.23
	0.05	13	0.08	0.35
	0.10	5	0.09	0.38
	0.20	3	0.11	0.54
0.75	Nil	> 50	0.43	0.06
	0.01	> 50	0.14	0.05
	0.025	> 50	0.10	0.07
	0.05	> 50	0.10	0.07
	0.10	5	0.10	0.44
	0.20	6	0.16	0.77
1.0	Nil	> 50	0.45	0.08
	0.01	> 50	0.16	0.07
	0.025	> 50	0.19	0.04
	0.05	> 50	0.11	0.06
	0.10	> 50	0.10	0.11
	0.20	> 50	0.09	0.14

* "Fluidity" is assessed as the number of days for which the latex is maintained in a fluid condition.

These results show that by having the enzyme present during fermentation the concentration can be markedly reduced. Thus only 0.05% was required to reduce the nitrogen to about 0.1% and ash to about 0.08%. Also since the presence of the enzyme during fermentation destabilises the latex, it is necessary to have a surface active agent as a stabilizer (Nonidet-P40) present to keep the system fluid; the optimum concentration needed of surface active agent to maintain fluidity is about 0.75%. 5

EXAMPLE 6

A pilot scale fermentor containing about 500 litres of latex was set up to evaluate the technological properties of the resulting rubber. Fresh latex was ammoniated to pH 9.5 and further treated with 0.75% Nonidet-P40 and 0.05% Alcalase as in Example 5. From the eighth day onwards a seventh of the bulk was withdrawn from the fermentor daily and the volume replaced by a batch of fresh field latex ammoniated to pH 9.5 and further treated with 0.75% Nonidet-P40 and 0.05% Alcalase. The practice was continued for more than 200 days. At various intervals the withdrawn samples were tested for technological properties. A summary of the result is given in Table 6. The raw rubber properties, with the exception of plasticity retention index (PRI) were either comparable or better than that of the SMR 5 control. PRI was relatively poor but was improved to normal level by dipping the crumbs in a mixture of oxalic acid and thiourea, while the cure behaviour and the vulcanisate properties were similar to that of the SMR 5 control, the dynamic properties, particularly the heat build-up properties, were much better. 10 15

TABLE 6

Property	Control Sample (SMR 5L)	Time from start bulking cycle (days)							
		0	3	7	10	20	30	50	
Tensile strength, MN. m ²	25.1	25.9	23.5	24.7	25.4	26.0	26.8	23.5	
Elongation at break, %	450	440	500	460	480	470	480	450	
M300 MN, m ²	15.0	15.5	11.0	11.0	14.0	13.5	14.5	13.7	
Hardness MN, m ²	65	64	62	63	65	61	60	62	
Resilience	69.2	68.2	72	68.9	68.3	72.6	72.4	71.7	
Compression set	10.7	9	10	9.8	9.2	9.1	9.4	10.1	
Scorch time	6.3	5.6	6.7	6.8	6.5	6.3	6.3	5.9	
Optimum cure time, t90	48.5	50.3	54.4	46.3	48.5	48.3	45.0	42.0	
Good rich heat build-up									
25 mins.	20.3	20.0	16.5	16.2	—	17.0	16.5	17.8	
60 mins.	24.1	22.8	18.1	17.3	—	18.9	17.9	21.5	
120 mins.	31.6	27.1	21.1	19.3	—	21.0	20.5	23.7	

CLAIMS

1. A method of producing solid coagulated natural rubber which comprises:
 1. ammoniating field latex to a pH of at least 9.0;
 2. stabilizing the ammoniated latex with a nonionic surface active agent;
 - 5 3. fermenting the ammoniated latex for a period of at least 3 days under anaerobic conditions; 5
 4. before, or during fermentation treating the ammoniated, stabilized latex with at least one proteolytic enzyme;
 5. during the fermentation and enzymatic treatment maintaining the pH of the latex at at least 9.0 if necessary by further additions of ammonia;
 - 10 6. optionally, diluting the fermented and enzymatically treated latex with water; and 10
 7. coagulating the latex with acid.
2. A method as claimed in claim 1 wherein the field latex is ammoniated to and maintained at a pH of about 9.5.
3. a method as claimed in either claim 1 or claim 2 wherein the latex is fresh field latex.
- 15 4. A method as claimed in any one of claims 1 to 3 wherein the nonionic surface active agent is a 15
condensation product of an alkylene oxide with a lipophilic component.
5. A method as claimed in any one of claims 1 to 4 wherein the amount of proteolytic enzyme used is from 0.01 to 0.03% of 100% active enzyme by weight on the dry rubber content of the latex.
6. A method as claimed in any one of claims 1 to 5 which comprises the steps of:
 - 20 1. bulking a portion of freshly tapped field latex which has been ammoniated to a pH of at least 9.0, 20
stabilized with a non-ionic surface active agent and treated with a proteolytic enzyme;
 2. repeating step 1 on a daily basis for at least 5 and preferably 7 days thereby allowing the bulked latex to ferment;
 3. maintaining the pH of the bulked latex at at least 9.0, if necessary by adding further ammonia;
 - 25 4. on a subsequent day, removing from the fermented bulk a portion of the latex and coagulating 25
it, optionally after dilution, with acid, and replacing the latex removed from the bulk with a further portion of freshly tapped field latex treated according to step 1; and
 5. repeating step 4 on a daily basis.
7. A method as claimed in any one of claims 1 to 5 which comprises the steps of:
 - 30 1. bulking a quantity of at least 5 and preferably 7 portions of latex which has been ammoniated to 30
a pH of at least 9.0, stabilized with a non-ionic surface active agent and treated with a proteolytic enzyme;
 2. holding the bulked latex for at least the same number of days as portions of latex in it, thereby allowing the latex to ferment;
 - 35 3. maintaining the pH of the latex at at least 9.0, if necessary by adding further ammonia; 35
 4. on a subsequent day, removing from the fermented bulk a portion of the latex and coagulating it, optionally after dilution, with acid, and replacing the latex removed from the bulk with a portion of freshly tapped field latex treated according to step 1; and
 5. repeating step 4 on a daily basis.